

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for Manufacture of Intermediates for Pigments and Dyestuffs

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

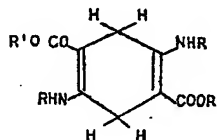
This invention relates to a process for manufacture of intermediates for pigments and dyestuffs and more particularly to a process for the manufacture of 2:5-bis-(arylamino)terephthalic esters.

In the Annalen, volume 404, page 301 a method is described whereby diethyl 3:6-dihydro-2:5-bis-(arylamino)terephthalates and certain derivatives thereof may be dehydrogenated to the corresponding fully aromatic diethyl 2:5-bis-(arylamino)terephthalates by boiling an alcoholic solution with iodine. It is stated also that dehydrogenation of such compounds takes place very slowly when they are heated to the melting point in presence of air.

We have now found that 3:6-dihydro-2:5-bis-(arylamino)terephthalic esters may be dehydrogenated by a process which not only gives higher yields of 2:5-bis-(arylamino)terephthalic esters than are obtainable by the known processes but is applicable to the preparation of a wider range of substituted derivatives of 2:5-bis-(arylamino)terephthalic esters. Furthermore the new process does not involve the use of the expensive element iodine.

According to the invention we provide a process for the manufacture of 2:5-bis-(arylamino)terephthalic esters which comprises treating a 3:6-dihydro-2:5-bis-(arylamino)-

terephthalic ester which in one of its tautomeric forms has the formula



wherein R represents a carbocyclic or heterocyclic aromatic residue which may be substituted or may form part of a polycyclic structure, and R' represents a lower alkyl group, with a quinone.

As examples of homocyclic or heterocyclic residues which may be represented by R there may be mentioned phenyl, naphthyl, pyrenyl, pyridyl, carbazyl and dibenzfuranyl.

As examples of substituents which may be present in the carbocyclic or heterocyclic residues there may be mentioned halogeno such as chloro and bromo; alkyl such as methyl and ethyl; substituted alkyl such as trifluoromethyl; aryl such as phenyl and p-tolyl; arylamino such as anilino; acylamido such as acetylamido, benzoylamido and p-toluenesulphonamido; alkoxy such as methoxy, ethoxy and β -hydroxyethoxy and aryloxy such as phenoxy and cresoxy.

By the term "lower alkyl group", we mean an alkyl group of not more than 5 carbon atoms and as examples of such groups which may be represented by R' there may be mentioned methyl ethyl, propyl, butyl and amyl.

As examples of quinones which may be used in the process of the invention there may be mentioned benzoquinone, 1:4-

naphthoquinone, 1:2-naphthoquinone, chloranil, bromanil, 2:5-dihydroxybenzoquinone, 2:3-dicyano-5:6-dichlorobenzoquinone, anthraquinone, 2:6-dihydroxyanthraquinone and acenaphthenequinone.

The process of the invention may be carried out by heating (for example at the boiling point) a mixture of the 3:6-dihydro-2:5-bis(arylamino)terephthalic ester and the quinone in a suitable organic solvent such as an alcohol, for example ethyl alcohol, amyl alcohol or ethylene glycol, dimethylformamide or a halogenated aromatic compound for example monochlorobenzene or *o*-dichlorobenzene. Especially high yields of 2:5-bis(arylamino)terephthalic esters are obtained when monochlorobenzene is used as solvent. The products may usually be isolated by crystallisation from the solvent used, followed by filtration and washing. In some cases the hydroquinone corresponding to the particular quinone used crystallises out first and may be removed by filtration, and the 2:5-bis(arylamino)terephthalic ester may subsequently be isolated by evaporation to dryness.

As examples of 3:6-dihydro-2:5-bis(arylamino)terephthalic esters which may be used in the process of the invention there may be mentioned dimethyl 3:6-dihydro-2:5-bis(phenylamino)terephthalate, dimethyl 3:6-dihydro-2:5-bis-(2¹:4¹-dichlorophenylamino)terephthalate, dimethyl 3:6-dihydro-2:5-bis-(2¹-methoxyphenylamino)terephthalate, dimethyl 3:6-dihydro-2:5-bis-(4¹-methoxyphenylamino)terephthalate, dimethyl 3:6-dihydro-2:5-bis-(2¹:5¹-dichlorophenylamino)terephthalate, dimethyl 3:6-dihydro-2:5-bis-(4¹-acetylaminophenylamino)terephthalate, dimethyl 3:6-dihydro-2:5-bis-(4¹-phenylaminophenylamino)terephthalate, dimethyl 3:6-dihydro-2:5-bis-(pyridyl-2¹-amino)terephthalate, dimethyl 3:6-dihydro-2:5-bis(β-naphthylamino)terephthalate and dimethyl 3:6-dihydro-2:5-bis(pyrenyl-1¹-amino)terephthalate.

We have further found that by a modification of the process of the invention it is possible to accomplish virtually complete dehydrogenation of a 3:6-dihydro-2:5-diarylamino-terephthalic ester by treatment with a very small amount of a quinone.

According to a further feature of the invention we provide a modified process for the manufacture of 2:5-bis(arylamino)terephthalic esters which comprises treating a 3:6-dihydro-2:5-bis(arylamino)terephthalic ester of the above formula wherein R and R¹ have the meaning stated above with less than the chemically equivalent quantity of a quinone in an organic liquid through which a current of air or oxygen is passed.

The modified process of the invention may conveniently be carried out by passage of a

current of air or oxygen through a hot (for example boiling) solution or suspension of the 3:6-dihydro-2:5-bis(arylamino)terephthalic ester and a small amount (for example 0.01 of an equivalent) of the quinone in an organic liquid such as an alcohol, for example ethyl alcohol, amyl alcohol or ethylene glycol, dimethyl formamide or a halogenated aromatic compound, for example monochlorobenzene or dichlorobenzene. The products may be isolated as described above.

In carrying out the process or the modified process of the invention we prefer to use quinones which are substituted by negative radicals such as halogen atoms, hydroxy groups or cyano-groups and especially we prefer to use chloranil.

By means of the process or the modified process of the invention 2:5-bis(arylamino)terephthalic esters may be obtained in high yield and in a reasonable state of purity.

The products are useful in the manufacture of pigments and dyestuffs and particularly in the manufacture of *lin*-quinacridones.

The invention is illustrated but not limited by the following Examples in which the parts are by weight.

EXAMPLE 1

A suspension of 1.9 parts of dimethyl-3:6-dihydro-2:5-bis-(phenylamino)terephthalate and 1.25 parts of chloranil in 20 parts of technical amyl alcohol is stirred at the boil under reflux for 1 hour. The deep orange solution so obtained is cooled and the dimethyl-2:5-bis(phenylamino)terephthalate which separates in bright orange needles is filtered off and dried. 1.67 parts of the product are obtained, having a melting point of from 155° C. to 162° C.

EXAMPLE 2

In place of the 20 parts of amyl alcohol used in Example 1, there are used 20 parts of monochlorobenzene. After boiling for 10 minutes a clear orange-red solution is obtained. The almost colourless needles of tetrachloro-hydroquinone which separate on cooling are filtered off and washed with 5 parts of chlorobenzene. The chlorobenzene filtrate and washings are combined and evaporated to dryness and the residue of bright orange needles is slurried with 15 parts of ethanol, filtered and dried. 1.7 parts of dimethyl-2:5-bis-(phenylamino)terephthalate are thereby obtained having a melting point of from 154° C. to 156° C.

EXAMPLE 3

A current of dry air is bubbled through a stirred boiling suspension of 1.9 parts of dimethyl-3:6-dihydro-2:5-bis-(phenylamino)terephthalate and 0.125 part of chloranil (0.1 equivalents) in 20 parts of technical amyl alcohol for 4 hours. The solid material gradually dissolves to form a deep orange solution. On cooling dimethyl-2:5-bis-(phenylamino)terephthalate crystallises out in

bright orange needles which are filtered off, washed with a little ethyl alcohol and dried. 1.5 parts of the product are obtained, having a melting point of from 153° C. to 160° C.

EXAMPLE 4

5.2 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (2¹:4¹ - dichlorophenylamino)terephthalate and 2.5 parts of chloranil are stirred at the boil with 45 parts of dimethylformamide for 1 hour. The mixture is cooled, and the crystals of dimethyl-2:5-bis-(2¹:4¹-dichlorophenylamino)terephthalate which separate are filtered off, washed with a little dimethyl formamide and ethanol and then dried. 3.9 parts of the product are obtained, having a melting point of 297° C.

EXAMPLE 5

5 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (2¹-methoxyphenylamino)terephthalate are suspended in 100 parts of boiling ethanol, 2.9 parts of chloranil are added and the mixture is stirred and boiled under reflux for 45 minutes. The pale orange crystals of the dihydro derivative dissolve and bright scarlet needles of the reaction product separate. The suspension is cooled, filtered, the scarlet crystals washed with 25 parts of warm ethanol and dried at 100° C. 4.4 parts of dimethyl-2:5 - bis - (2¹ - methoxyphenylamino)terephthalate are obtained having a melting point of from 168° C. to 169° C.

EXAMPLE 6

2.5 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (2¹:5¹ - dichlorophenylamino)terephthalate are dissolved in 50 parts of dimethyl formamide at between 120° C. and 130° C. To the pale orange solution are added 1.2 parts of chloranil and the mixture is boiled under reflux for 5 minutes. The resulting deep orange-red solution is cooled and the orange needles of dimethyl - 2:5 - bis - (2¹:5¹-dichlorophenylamino)terephthalate which separate are filtered off, washed with 100 parts of warm methanol and dried at 100° C. 2.0 parts of the product are obtained, having a melting point of from 296° C. to 298° C.

EXAMPLE 7

A solution of 19.8 parts of chloranil in 200 parts of dimethyl formamide is added rapidly, with stirring to a suspension of 38.7 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (4¹ - acetylaminophenylamino)terephthalate at between 120° C. and 130° C. in 300 parts of dimethyl formamide. After boiling under reflux for 10 minutes the deep orange-yellow solution is cooled and the orange crystals of dimethyl-2:5-bis-(4¹-acetylaminophenylamino)terephthalate which separate are filtered off, and washed with methanol. 33.5 parts of the product are obtained, having a melting point of from 306° C. to 309° C.

The dimethyl - 3:6 - dihydro - 2:5 - bis - (p - acetaminophenylamino)terephthalate used in this Example may be obtained by reacting

35 parts of p-aminoacetanilide with 22.8 parts of dimethylsuccinosuccinate in a boiling mixture of 200 parts of ethanol and 100 parts of glacial acetic acid. The mixture is refluxed for 90 minutes and the orange-yellow precipitate is filtered from the hot solution, washed with ethanol and dried.

EXAMPLE 8

A solution of 2.5 parts of chloranil in 25 parts of hot dimethyl formamide is added rapidly to a stirred suspension of 5.6 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (4¹-phenylaminophenylamino)terephthalate in 25 parts of dimethyl formamide at between 120° C. and 130° C. The resulting mixture is boiled under reflux for 5 minutes. The deep red solution so obtained is evaporated to about one third of its original volume, and 50 parts of methanol are added. On standing at room temperature dimethyl - 2:5 - bis - (4¹ - phenylaminophenylamino)terephthalate crystallises in crimson needles, which are filtered off, and washed with methanol. 4.6 parts of the product are obtained, having a melting point of between 218° C. and 220° C.

The dimethyl - 3:6 - dihydro - 2:5 - bis - (4¹ - phenylaminophenylamino)terephthalate used in this Example may be obtained by boiling under reflux for 2 hours a mixture of 36.8 parts of p-aminodiphenylamine, 22.8 parts of dimethyl-succino-succinate, 300 parts of ethanol and 150 parts of glacial acetic acid. It is a light purple powder of melting point from 235° C. to 240° C.

EXAMPLE 9

A solution of 9.6 parts of chloranil in 50 parts of hot ethylene glycol is added rapidly to a stirred suspension of 13 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (pyridyl-2¹-amino)terephthalate in 100 parts of boiling ethylene glycol. The mixture is stirred and boiled under reflux for 5 minutes, and the bright scarlet solution which forms is cooled. The scarlet needles of dimethyl-2:5-bis-(pyridyl-2¹-amino)terephthalate which separate are filtered off, washed with 200 parts of ethanol and dried at 100° C. 12 parts of the product are obtained, having a melting point above 340° C.

The dimethyl - 3:6 - dihydro - 2:5 - bis - (pyridyl-2¹-amino)terephthalate used in this Example may be prepared as follows:—

A solution of 22.8 parts of dimethyl succino succinate and 28.5 parts of 2-aminopyridine in 140 parts of glacial acetic acid is stirred and boiled under reflux in an atmosphere of nitrogen for 12 hours. The pale yellow crystalline precipitate which slowly separates is filtered from the hot mixture, washed with methanol and dried.

EXAMPLE 10

2.5 parts of chloranil are added to a stirred suspension of 4.8 parts of dimethyl-3:6-dihydro - 2:5 - bis - (β - naphthylamino)terephthalate in 30 parts of boiling dimethyl

formamide. After boiling under reflux for 3 minutes the deep red solution is cooled to about 60° C. and diluted with an equal volume of methanol. The scarlet plates of dimethyl - 2:5 - bis - (β - naphthylamino)-terephthalate which separate are filtered off, and washed with methanol. 3.6 parts of the product are obtained, having a melting point of from 228° C. to 230° C.

If the 30 parts of dimethyl formamide used in this Example are replaced by 75 parts of 2-ethoxyethanol, 3.2 parts of dimethyl-2:5-bis - (β - naphthylamino)-terephthalate are obtained.

EXAMPLE 11

A brisk current of air is blown through a boiling suspension of 4.78 parts of dimethyl-3:6 - dihydro - 2:5 - bis - (β - naphthylamino)terephthalate and 0.28 part of chloranil in 50 parts of amyl alcohol. After boiling under reflux for 4 hours the mixture is cooled and the bright orange crystals of dimethyl-2:5-bis-(β - naphthylamino)terephthalate are filtered off, washed with ethanol and dried. 3.0 parts of the product are obtained, having a melting point of from 238° C. to 240° C.

EXAMPLE 12

A brisk current of air is blown through a stirred suspension of 3.78 parts of dimethyl-3:6 - dihydro - 2:5 - bis - (phenylamino)-terephthalate and 0.23 part of 2:3-dichloro-1:4-naphthoquinone in 50 parts of boiling amyl alcohol for 4 hours. The deep orange solution is cooled and the orange needles of dimethyl - 2:5 - bis - (phenylamino)terephthalate which separate are filtered off, washed with ethanol and dried. 2.7 parts of the product are obtained, having a melting point of from 150° C. to 153° C.

EXAMPLE 13

A brisk current of air is blown through a suspension of 3.78 parts of dimethyl-3:6-dihydro - 2:5 - bis - (phenylamino) - terephthalate and 0.025 part of chloranil (0.01 equivalents) in 40 parts of boiling amyl alcohol for 6 hours. The deep orange solution is cooled in ice and the bright orange-red needles of 2:5 - bis - (phenylamino)terephthalate which separate are filtered off, washed with methanol and dried. 3.1 parts of the product are obtained, having a melting point of from 153° C. to 156° C.

EXAMPLE 14

A mixture of 3.78 parts of dimethyl-3:6-dihydro - 2:5 - bis - (phenylamino)terephthalate and 0.025 part (0.01 equivalents) of chloranil in 75 parts of monochlorobenzene is stirred and boiled under reflux for 3 hours during which time a brisk current of air is blown through the solution. The product is isolated as described in Example 2. 3.2 parts of dimethyl - 2:5 - bis - (phenylamino)terephthalate are obtained, of melting point from 158° C. to 160° C.

EXAMPLE 15

10 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (4^1 - methoxyphenylamino)terephthalate are suspended in 150 parts of boiling ethanol and a solution of 5.8 parts of chloranil in 50 parts of hot ethanol is added. After boiling under reflux with stirring for 1 hour, the deep orange solution is cooled. Dimethyl - 2:5 - bis - (4^1 - methoxyphenylamino)terephthalate separates in bright scarlet needles, which are filtered off, washed with methanol and dried. 9.8 parts of the product are obtained, having a melting point of from 212° C. to 214° C.

EXAMPLE 16

A solution of 2.1 parts of diethyl 3:6-dihydro - 2:5 - bis(phenylamino)terephthalate and 0.125 parts (0.1 equivalents) of chloranil in 20 parts of technical amyl alcohol is stirred at the boil for 1 hour, while a steady stream of dry oxygen is passed through the boiling solution. On cooling orange red crystals of diethyl 2:5 - bis - (phenylamino)terephthalate separate which are filtered off and dried. 1.77 parts of the product are obtained, having a melting point of from 140° to 144° C.

EXAMPLE 17

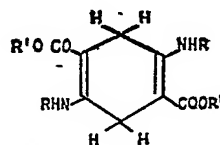
A suspension of 3.78 parts of dimethyl-3:6 - dihydro - 2:5 - bis - (phenylamino)-terephthalate and 1.08 parts of benzoquinone in 40 parts of ethyl alcohol is stirred at the boil under reflux for 4 hours. The solution is filtered and on cooling deposits crystals of dimethyl 2:5 - bis(phenylamino)terephthalate, melting point 156° to 159° C.

EXAMPLE 18

In place of 0.125 parts of chloranil in Example 3 there is used a stoichiometrically equivalent amount of 1:2-naphthoquinone, acenaphthene quinone, anthraquinone, 2:5-dihydroxybenzoquinone or 2:6 - dihydroxyanthraquinone. In each case a good yield of dimethyl 2:5 - bis - (phenylamino)terephthalate is obtained.

EXAMPLE 19

The following table summarises the conditions used for dehydrogenating various dihydro - 2:5 - bis - (arylamino)terephthalic esters of the formula



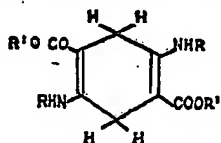
wherein R^1 stands for methyl. In each case the reaction mixture was boiled under reflux for 3 hours, with or without passage of air as indicated in column 3.

R	Melting-point of starting material	Moles of chloranil per mole of starting material	Organic Liquid	Whether air current passed	Melting-point of product
1. 3-chlorophenyl	212—217°C.	0.12	amyl alcohol	yes	150—152°C.
2. 4-chlorophenyl	243—248°C.	0.15	"	"	230—231°C.
3. 2-chlorophenyl	232—234°C.	0.13	"	"	194—196°C.
4. 2-methylphenyl	225—230°C.	0.11	"	"	208—212°C.
5. 3-methylphenyl	206—214°C.	0.125	"	"	150—155°C.
6. 4-methylphenyl	262—270°C.	0.106	"	"	220—225°C.
7. 5-chloro-2-methylphenyl	250—260°C.	0.13	"	"	250—258°C.
8. 4-chloro-2-methylphenyl	254—260°C.	0.14	"	"	258—262°C.
9. 5-chloro-2-methoxyphenyl	200—205°C.	0.14	"	"	258—265°C.
10. 1-naphthyl	260—265°C.	0.1	chlorobenzene	"	—
11. 1-pyrenyl	above 330°C.	1.0	"	no	above 330°C.
12. 1-chloro-2-naphthyl	—	1.0	"	no	202—203°C.
13. 5:8-dichloro-1-naphthyl	—	1.0	"	no	330°C.
14. 2-methyl-1-naphthyl	251—255°C.	0.1	"	yes	280°C.

5 The dimethyl - 3:6 - dihydro - 2:5 - bis-(arylamino)terephthalates in the above table may all be obtained by condensation of dimethyl succinylsuccinate with the appropriate amine. Numbers 1, 2, 3, 4, 5, 6 and 10 11 may be obtained by condensation in a boiling mixture of 2 parts of ethanol with one part of acetic acid, and the remaining compounds may be obtained by condensation in boiling ethanol containing a little concentrated aqueous hydrochloric acid.

WHAT WE CLAIM IS:—

15 1. A process for the manufacture of 2:5-bis-(arylamino)terephthalic esters which comprises treating a 3:6 - dihydro - 2:5 - bis-(arylamino)terephthalic ester which in one of its tautomeric forms has the formula



wherein R represents a carbocyclic or heterocyclic aromatic residue which may be substituted or may form part of a polycyclic structure, and R¹ represents a lower alkyl group, with a quinone. 20

2. Process for the manufacture of 2:5-bis-(arylamino)terephthalic esters which comprises treating a 3:6-dihydro-2:5-bis-(arylamino)-terephthalic ester of the above formula wherein R and R¹ have the meaning stated above with less than the chemically equivalent quantity of a quinone in an organic liquid through which a current of air or oxygen is passed. 25 30

3. Process according to Claim 1 or 2 wherein the quinone is substituted by negative radicals. 35

4. Process according to Claims 1 or 2 wherein the quinone is chloranil.

5. 2:5 - bis - (arylamino)terephthalic esters whenever made by the process of any of Claims 1—4. 40

6. Process for the manufacture of 2:5-bis - (arylamino)terephthalic esters as herein-

before particularly described, especially with reference to the foregoing Examples.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Process for Manufacture of Intermediates for Pigments and Dyestuffs

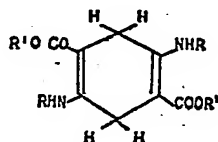
We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to a process for manufacture of intermediates for pigments and dyestuffs and more particularly to a process for the manufacture of 2:5-bis-(arylamino)terephthalic esters.

In the *Annalen*, volume 404, page 301 a method is described whereby 3:6-dihydro-2:5-bis-(arylamino)terephthalic esters and certain derivatives thereof may be dehydrogenated to the corresponding fully aromatic 2:5-bis-(arylamino)terephthalic esters by boiling an alcoholic solution with iodine. It is stated also that dehydrogenation of such compounds takes place very slowly when they are heated to the melting point in presence of air.

We have now found that 3:6-dihydro-2:5-bis-(arylamino)terephthalic esters may be dehydrogenated by a process which not only gives higher yields of 2:5-bis-(arylamino)terephthalic esters than are obtainable by the known processes but is applicable to the preparation of a wider range of substituted derivatives of 2:5-bis-(arylamino)terephthalic esters. Furthermore the new process does not involve the use of the expensive element iodine.

According to the invention we provide a process for the manufacture of 2:5-bis-(arylamino)terephthalic esters which comprises treating a 3:6-dihydro-2:5-bis-(arylamino)terephthalic ester which in one of its tautomeric forms has the formula



wherein R represents a homocyclic or heterocyclic aromatic residue which may be monocyclic or polycyclic and may be substituted, and R¹ represents a lower alkyl group, with a quinone.

As examples of homocyclic or heterocyclic residues which may be represented by R there may be mentioned phenyl, naphthyl, pyridyl, carbazyl and dibenzfuranyl.

As examples of substituents which may be

present in the homocyclic or heterocyclic residues there may be mentioned halogens such as chloro and bromo; alkyl such as methyl and ethyl; substituted alkyl such as trifluoromethyl; aryl such as phenyl and p-tolyl; arylamino such as anilino; acylamido such as acetylamido, benzoylamido and p-toluenesulphonamido; alkoxy such as methoxy, ethoxy and β -hydroxyethoxy and aryl-oxy such as phenoxy and cresoxy.

As examples of lower alkyl groups which may be represented by R¹ there may be mentioned methyl and ethyl.

The process of the invention may be carried out by heating (for example at the boiling point) a mixture of the 3:6-dihydro-2:5-bis-(arylamino)terephthalic ester and the quinone in a suitable organic solvent such as an alcohol, for example ethyl alcohol, amyl alcohol and ethylene glycol, dimethylformamide or a halogenated aromatic compound for example monochlorobenzene or o-dichlorobenzene. Especially high yields of 2:5-bis-(arylamino)terephthalic esters are obtained when monochlorobenzene is used as solvent. The products may usually be isolated by crystallisation from the solvent used, followed by filtration and washing. In some cases the hydroquinone corresponding to the particular quinone used crystallises out first and may be removed by filtration, and the 2:5-bis-(arylamino)terephthalic ester may subsequently be isolated by evaporation to dryness.

As examples of 3:6-dihydro-2:5-bis-(arylamino)terephthalates which may be used in the process of the invention there may be mentioned dimethyl-3:6-dihydro-2:5-bis-(phenylamino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(2¹,4¹-dichlorophenylamino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(2¹-methoxyphenylamino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(4¹-methoxyphenylamino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(2¹,5¹-dichlorophenylamino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(4¹-acetylaminophenylamino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(4¹-phenylaminophenylamino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(pyridyl-2¹-amino)terephthalate, dimethyl-3:6-dihydro-2:5-bis-(β -naphthylamino)terephthalate.

We have further found that by a modification of the process of the invention it is possible to accomplish virtually complete

dehydrogenation of a 3:6-dihydro-2:5-diarylamino-terephthalic ester by treatment with a very small amount of a quinone.

According to a further feature of the invention we provide a modified process for the manufacture of 2:5 - bis(arylamino)terephthalic esters which comprises treating a 3:6 - dihydro - 2:5 - bis(arylamino)terephthalic ester of the above formula wherein R and R¹ have the meaning stated above with less than the chemically equivalent quantity of a quinone in an organic solvent through which a current of air is passed.

The modified process of the invention may conveniently be carried out by passage of a current of air through a hot (for example boiling) solution or suspension of the 3:6-dihydro - 2:5 - bis(arylamino)terephthalic ester and a small amount (for example 0.01 of an equivalent) of the quinone in a suitable organic solvent such as an alcohol, for example ethyl alcohol, amyl alcohol or ethylene glycol, dimethyl formamide or a halogenated aromatic compound, for example monochlorobenzene or dichlorobenzene. The products may be isolated as described above.

In carrying out the process or the modified process of the invention we prefer to use 1:4-benzoquinones or 1:4-naphthoquinones which are substituted by negative radicals such as halogen atoms, and especially we prefer to use chloranil.

By means of the process or the modified process of the invention 2:5 - bis - (arylamino)terephthalic esters may be obtained in high yield and in a reasonable state of purity.

The products are useful in the manufacture of pigments and dyestuffs and particularly in the manufacture of *lin*-quinacridones.

The invention is illustrated but not limited by the following Examples in which the parts are by weight.

EXAMPLE 1

A suspension of 1.9 parts of dimethyl-3:6-dihydro - 2:5 - bis - (phenylamino)terephthalate and 1.25 parts of chloranil in 20 parts of technical amyl alcohol is stirred at the boil under reflux for 1 hour. The deep orange solution so obtained is cooled and the dimethyl - 2:5 - bis(phenylamino)terephthalate which separates in bright orange needles is filtered off and dried. 1.67 parts of the product are obtained, having a melting point of from 155° C. to 162° C.

EXAMPLE 2

In place of the 20 parts of amyl alcohol used in Example 1, there are used 20 parts of monochlorobenzene. After boiling for 10 minutes a clear orange-red solution is obtained. The almost colourless needles of tetrachloro-hydroquinone which separate on cooling are filtered off and washed with 5 parts of chlorobenzene. The chlorobenzene filtrate and washings are combined and evaporated to dryness and the residue of bright orange needles is

slurried with 15 parts of ethanol, filtered and dried. 1.7 parts of dimethyl-2:5-bis-(phenylamino)terephthalate are thereby obtained having a melting point of from 154° C. to 156° C.

EXAMPLE 3

A current of dry air is bubbled through a stirred boiling suspension of 1.9 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (phenylamino)terephthalate and 0.125 part of chloranil (0.1 equivalents) in 20 parts of technical amyl alcohol for 4 hours. The solid material gradually dissolves to form a deep orange solution. On cooling dimethyl-2:5-bis-(phenylamino)terephthalate crystallises out in bright orange needles which are filtered off, washed with a little ethyl alcohol and dried. 1.5 parts of the product are obtained, having a melting point of from 153° C. to 160° C.

EXAMPLE 4

5.2 parts of dimethyl - 3:6 - dihydro-2:5 - bis - (2¹:4¹ - dichlorophenylamino)terephthalate and 2.5 parts of chloranil are stirred at the boil with 45 parts of dimethyl-formamide for 1 hour. The mixture is cooled, and the crystals of dimethyl - 2:5 - bis - (2¹ : 4¹ - dichlorophenylamino)terephthalate which separate are filtered off, washed with a little dimethyl formamide and ethanol and then dried. 3.9 parts of the product are obtained, having a melting point of 297° C.

EXAMPLE 5

5 parts of dimethyl - 3:6 - dihydro - 2:5-bis-(2¹-methoxyphenylamino)terephthalate are suspended in 100 parts of boiling ethanol, 2.9 parts of chloranil are added and the mixture is stirred and boiled under reflux for 45 minutes. The pale orange crystals of the dihydro derivative dissolve and bright scarlet needles of the reaction product separate. The suspension is cooled, filtered, the scarlet crystals washed with 25 parts of warm ethanol and dried at 100° C. 4.4 parts of dimethyl - 2:5 - bis - (2¹ - methoxyphenylamino)terephthalate are obtained having a melting point of from 168° C. to 169° C.

EXAMPLE 6

2.5 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (2¹:5¹ - dichlorophenylamino)terephthalate are dissolved in 50 parts of dimethyl formamide at between 120° C. and 130° C. To the pale orange solution are added 1.2 parts of chloranil and the mixture is boiled under reflux for 5 minutes. The resulting deep orange-red solution is cooled and the orange needles of dimethyl-2:5-bis-(2¹ : 5¹ - dichlorophenylamino)terephthalate which separate are filtered off, washed with 100 parts of warm methanol and dried at 100° C. 2.0 parts of the product are obtained, having a melting point of from 296° C. to 298° C.

EXAMPLE 7

A solution of 19.8 parts of chloranil in 200 parts of dimethyl formamide is added rapidly, with stirring to a suspension of 38.7 parts of

dimethyl - 3:6 - dihydro - 2:5 - bis - (4¹-acetylaminophenylamino)terephthalate at between 120° C. and 130° C. in 300 parts of dimethyl formamide. After boiling under reflux for 10 minutes the deep orange-yellow solution is cooled and the orange crystals of dimethyl - 2:5 - bis - (4¹ - acetylaminophenylamino)terephthalate which separate are filtered off, and washed with methanol. 33.5 parts of the product are obtained, having a melting point of from 306° C. to 309° C.

The dimethyl - 3:6 - dihydro - 2:5 - bis - (p-acetaminophenylamino)terephthalate used in this Example may be obtained by reacting 35 parts of p-aminoacetanilide with 22.8 parts of dimethylsuccinosuccinate in a boiling mixture of 200 parts of ethanol and 100 parts of glacial acetic acid. The mixture is refluxed for 90 minutes and the orange-yellow precipitate is filtered from the hot solution, washed with ethanol and dried.

EXAMPLE 8

A solution of 2.5 parts of chloranil in 25 parts of hot dimethyl formamide is added rapidly to a stirred suspension of 5.6 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (4¹-phenylaminophenylamino)terephthalate in 25 parts of dimethyl formamide at between 120° C. and 130° C. The resulting mixture is boiled under reflux for 5 minutes. The deep red solution so obtained is evaporated to about one third of its original volume, and 50 parts of methanol are added. On standing at room temperature dimethyl-2:5-bis-(4¹ - phenylaminophenylamino)terephthalate crystallises in crimson needles, which are filtered off, and washed with methanol. 4.6 parts of the product are obtained, having a melting point of between 218° C. and 220° C.

The dimethyl - 3:6 - dihydro - 2:5 - bis - (4¹ - phenylaminophenylamino)terephthalate used in this Example may be obtained by boiling under reflux for 2 hours a mixture of 36.8 parts of p-aminodiphenylamine, 22.8 parts of dimethyl-succino-succinate, 300 parts of ethanol and 150 parts of glacial acetic acid. It is a light purple powder of melting point from 235° C. to 240° C.

EXAMPLE 9

A solution of 9.6 parts of chloranil in 50 parts of hot ethylene glycol is added rapidly to a stirred suspension of 13 parts of dimethyl - 3:6 - dihydro - 2:5 - bis - (pyridyl - 2¹ - amino)terephthalate in 100 parts of boiling ethylene glycol. The mixture is stirred and boiled under reflux for 5 minutes, and the bright scarlet solution which forms is cooled. The scarlet needles of dimethyl-2:5-bis-(pyridyl - 2¹ - amino)terephthalate which separate are filtered off, washed with 200 parts of ethanol and dried at 100° C. 12 parts of the product are obtained, having a melting point above 340° C.

The dimethyl - 3:6 - dihydro - 2:5 - bis - (pyridyl - 2¹ - amino)terephthalate used in

this Example may be prepared as follows:—

A solution of 22.8 parts of dimethyl succino succinate and 28.5 parts of 2-amino-pyridine in 140 parts of glacial acetic acid is stirred and boiled under reflux in an atmosphere of nitrogen for 12 hours. The pale yellow crystalline precipitate which slowly separates is filtered from the hot mixture, washed with methanol and dried.

EXAMPLE 10

2.5 parts of chloranil are added to a stirred suspension of 4.8 parts of dimethyl-3:6-dihydro - 2:5 - bis - (β - naphthylamino)-terephthalate in 30 parts of boiling dimethyl formamide. After boiling under reflux for 3 minutes the deep red solution is cooled to about 60° C. and diluted with an equal volume of methanol. The scarlet plates of dimethyl - 2:5 - bis - (β - naphthylamino)-terephthalate which separate are filtered off, and washed with methanol. 3.6 parts of the product are obtained, having a melting point of from 228° C. to 230° C.

If the 30 parts of dimethyl formamide used in this Example are replaced by 75 parts of 2-ethoxyethanol, 3.2 parts of dimethyl-2:5-bis - (β - naphthylamino) - terephthalate are obtained.

EXAMPLE 11

A brisk current of air is blown through a boiling suspension of 4.78 parts of dimethyl-3:6 - dihydro - 2:5 - bis - (β - naphthylamino)terephthalate and 0.28 part of chloranil in 50 parts of amyl alcohol. After boiling under reflux for 4 hours the mixture is cooled and the bright orange crystals of dimethyl-2:5 - bis - (β - naphthylamino)terephthalate are filtered off, washed with ethanol and dried. 3.0 parts of the product are obtained, having a melting point of from 238° C. to 240° C.

EXAMPLE 12

A brisk current of air is blown through a stirred suspension of 3.78 parts of dimethyl-3:6 - dihydro - 2:5 - bis - (phenylamino)-terephthalate and 0.23 part of 2:3-dichloro-1:4-naphthoquinone in 50 parts of boiling amyl alcohol for 4 hours. The deep orange solution is cooled and the orange needles of dimethyl - 2:5 - bis - (phenylamino)terephthalate which separate are filtered off, washed with ethanol and dried. 2.7 parts of the product are obtained, having a melting point of from 150° C. to 153° C.

EXAMPLE 13

A brisk current of air is blown through a suspension of 3.78 parts of dimethyl-3:6-dihydro - 2:5 - bis - (phenylamino)terephthalate and 0.025 part of chloranil (0.01 equivalents) in 40 parts of boiling amyl alcohol for 6 hours. The deep orange solution is cooled in ice and the bright orange-red needles of 2:5 - bis - (phenylamino)terephthalate which separate are filtered off, washed with methanol and dried. 3.1 parts

of the product are obtained, having a melting point of from 153° C. to 156° C.

EXAMPLE 14

5 A mixture of 3.78 parts of dimethyl-3:6-dihydro - 2:5 - *bis* - (phenylamino)terephthalate and 0.025 part (0.01 equivalents) of chloranil in 75 parts of monochlorobenzene is stirred and boiled under reflux for 3 hours during which time a brisk current of air is
10 blown through the solution. The product is isolated as described in Example 2. 3.2 parts of dimethyl - 2:5 - *bis* - (phenylamino)terephthalate are obtained, of melting point from 158° C. to 160° C.

EXAMPLE 15

10 parts of dimethyl - 3:6 - dihydro-2:5-*bis* - (4¹ - methoxyphenylamino)terephthalate are suspended in 150 parts of boiling ethanol and a solution of 5.8 parts of chloranil in 50 parts of hot ethanol is added. After boiling under reflux with stirring for 1 hour, the deep orange solution is cooled. Dimethyl-2:5-*bis*-(4¹ - methoxyphenylamino)terephthalate separates in bright scarlet needles, which are filtered off, washed with methanol and dried.
25 9.8 parts of the product are obtained, having a melting point of from 212° C. to 214° C.

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